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CIRCULAR 199

# AROMATIC FLUORINE COMPOUNDS AS FUNGICIDES

BY

G. C. FINGER, FRANK H. REED, and LEO R. TEHON

*A summary of cooperative research by the Illinois State  
Geological Survey, the Illinois State Natural History Survey,  
and the United States Air Force, 1950-1954*



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## FOREWORD

The annual cost in the United States of the deterioration of materials is estimated at 12 billion dollars, and crop damage by plant disease at four billion. Agriculture in Illinois alone suffers a yearly loss of about 200 million dollars in decreased yield owing to plant disease. The armed services are confronted not only with the dollar cost of materials deterioration, but also with the possible loss of life by the use of such defective material.

A significant share of this cost is caused by fungus rot, mildew, and decay. The prevention of fungus action by chemical means has been rather limited in the past, and organic chemists are beginning to attack the problem with special synthetic compounds. Any chemical with high effectiveness in preventing fungus growth is called a fungicide.

Of the older and well-known fungicides, a number of inorganic fluorides have been particularly useful in wood treatment for the prevention of decay. The use of these fluorides or fluorine compounds in general is of special significance to the State of Illinois. Their manufacture is directly related to fluorspar (calcium fluoride), a strategic mineral in southern Illinois, which provides the fluorine for their industrial production.

When chemists at the State Geological Survey in 1949 prepared some new organic fluorides, and pathologists at the Natural History Survey discovered their fungicidal activity, a new field of fungicidal research was in the offing. To further explore the possibilities of aromatic fluorides as fungicides, a cooperative research program was operated by three governmental agencies during 1950-1954. The Geological Survey synthesized the test compounds, the Natural History Survey determined the fungicidal potency, and the Wright Air Development Center of the United States Air Force made special tests. We hope this information will stimulate further interest in the possibilities of aromatic fluorine compounds as fungicides and in fluorine research in general. The Geological Survey invites further inquiries.

John C. Frye

# AROMATIC FLUORINE COMPOUNDS AS FUNGICIDES

by

G. C. Finger, Frank H. Reed, and Leo R. Tehon\*

## ABSTRACT

More than 40 aromatic fluorine compounds were investigated. A concentration of 0.8 ppm of 1-fluoro-3-bromo-4,6-dinitrobenzene was found to cause complete growth stoppage of Aspergillus niger (a common mold) in the laboratory. Data are included on vinyl plastic and cotton fiber protection. Subsequent to the preceding investigations, additional work was accomplished by the Natural History Survey on gladiolus-disease control.

## INTRODUCTION

Fungus or mold action covers the deterioration, weakening, and destruction by rotting of cloth and other woven fabrics, leathers, plastics, wood, food, paint, and many other items during storage and use. Almost unbelievable is the extent of fungus etching of lenses or optical systems in scientific instruments, the growth of mold on insulation, causing electrical leakage, and the amazing ability of fungi to grow in desert and arctic areas.

It is obvious that the finding of an ideal or perfect chemical fungicide with such a tremendous range of uses is impossible. Some compounds lend only partial protection, others disintegrate quickly, others may cause staining, fiber-strength weakening, or corrosion of accessory parts, and still others may prove toxic to humans. Therefore, it is necessary to have available various fungicides from which may be chosen one or more, adapted to known or anticipated conditions.

Certain elements such as chlorine, bromine, and iodine of the halogen family have long been known to possess germicidal properties. Various types of organic compounds, notably those having benzene rings, such as phenol and cresols, are highly germicidal. With the introduction of chlorine into some of these ring compounds, the fungicidal capacity may be increased many times, as exemplified by the chlorinated phenols.

Fluorine, another halogen family element, might be presumed to confer some decided fungicidal activity upon its organic compounds. Unfortunately, the extreme reactivity of fluorine gas and the corrosiveness of hydrofluoric

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\*This publication was prepared after the death of Leo R. Tehon in October 1954, by Drs. Finger and Reed. Dr. Tehon discovered the fungicidal activity of fluorinated quinones in 1949 and was responsible for the screening program in the present study. He was formerly Head, Section of Applied Botany and Plant Pathology, Illinois State Natural History Survey.

acid, especially to glass, have given a most unfavorable impression of all fluorine compounds. Modern research has shown that only very few fluorine compounds exhibit these hazards.

The Division of Fluorine Chemistry of the Illinois State Geological Survey has been studying the substitution of fluorine in aromatic compounds since 1935. In some of these studies, compounds obtained were identical in structure to chlorine analogs having high fungicidal values. In 1949, five fluorinated benzoquinones with high fungistatic capacity to Macrosporium sarcinae-forme were found by the Section of Applied Botany and Plant Pathology of the Illinois State Natural History Survey. At this point the Air Force approached the two Surveys about an extended research program, and the present study on more than 40 fluorine compounds resulted. This is probably the first and most comprehensive investigation ever conducted exclusively on aromatic fluorine compounds as fungicides.

### Special Notes

The data presented are based almost entirely on laboratory findings, and it is not to be construed that the concentrations studied will be effective under field or other conditions.

Syntheses for the new compounds in table 1 are described in reports to the Air Force. These reports are available as official publications from the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C.

Anyone interested in the commercial phases of this subject is advised to review the patent literature. It is also advisable to consult Air Force officials at Wright Air Development Center as to the patent rights of the United States Government and the cooperating agencies on this research.

### Acknowledgments

This study was made possible by the financial assistance of the United States Air Force through the University of Illinois. A. E. Prince of the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, served as liaison scientist. Permission to use material from various Air Force reports and publications also is gratefully acknowledged. Credit is due two plant pathologists of the Natural History Survey, G. H. Boewe for Illinois crop-loss statistics, and J. L. Forsberg for information on his gladiolus disease studies with fluorine fungicides.

### THE CHEMICAL PROGRAM

The fluorine laboratories of the Illinois Geological Survey prepared the fluorine compounds, many of which are new. None of the compounds are commercially available, but some custom producers list a few of them.

### General Information

Aromatic fluorine chemistry may be defined as "the chemistry of the fluorinated benzene types of compounds." As fluorine is a member of the halogen



family, its compounds exhibit many characteristics in common with the chloro, bromo, and iodo analogs. Fluorine is also the unique member of its family; the derivatives frequently and unexpectedly lack certain family attributes, and yet may display most unusual properties.

Some general effects of fluorine substitution on physical properties are: very little change in boiling point; decreased surface tension, index of refraction, and heat of vaporization; increased vapor pressure; and irregular variations in melting points and solubilities. Other groups in the benzene molecule impose their own effects, but fluorine may modify them quite differently than do chlorine or the other halogens.

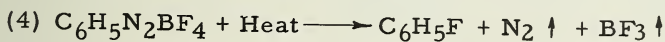
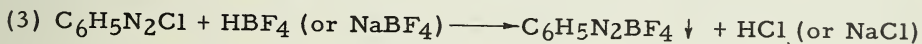
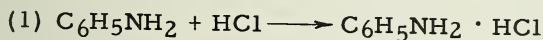
From a chemical-synthesis standpoint, fluorine is an ortho and para director in substitution reactions in the benzene ring. It does not usually interfere with the introduction of other groups by standard methods or cause any adverse effect upon the characteristic group reactions. For instance, fluorobenzene may be nitrated to the nitro derivative and this in turn reduced to fluoroaniline; then by the highly diversified diazotization reactions many other compounds can be made available.

In general, the fluorobenzene derivatives show greater stability than their chlorine analogs. But extreme cases of lability may occur, as in 2,4-dinitrofluorobenzene where the fluorine is about 600 times as reactive in alkaline solution as chlorine in the chlorine analog.

### Synthesis Considerations

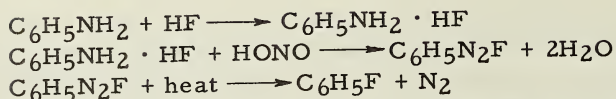
Fluorine is generally substituted into the benzene ring at a very early stage. Other groups are then introduced by standard methods well known to most organic chemists.

Laboratory syntheses. - A convenient laboratory method for introducing fluorine into the benzene ring is the Schiemann synthesis, or diazonium fluoborate process. The primary compound must be an aniline type, and the four-step process is illustrated by the preparation of fluorobenzene from aniline.



Steps (1) and (2) constitute the well-known diazotization process. Step (3) is the formation and isolation of the insoluble diazonium fluoborate as a dry salt which is stable to shock. Step (4) is the thermal decomposition of the dry salt to the aromatic fluoride and a gaseous mixture of nitrogen and boron trifluoride. Most decomposition temperatures are between 125° and 250° C. Over-all yields may be as high as 70%.

Industrial syntheses. - During World War II in Germany, fluorobenzene was being produced at a rate of 12 tons per month for the manufacture of DFDT, a fluorine insecticide analogous to DDT. The process involved the diazotization of aniline in a large volume of anhydrous hydrofluoric acid followed by a carefully controlled heating operation. The yield is 80% and better.



There is no doubt that the American chemical industry can operate this process, as it is already using tremendous tonnages of anhydrous hydrofluoric acid in petroleum, refrigerant, and atomic-energy operations.

### THE SCREENING PROGRAM

To determine fungistatic potency, three agar plate techniques - toxic agar dilution method, treatment of cotton fabric samples, and treatment of cotton thread - and four test fungi were used. Only those compounds showing high toxicity by the first procedure were given the second and third tests.

#### Test Fungi and Dilution Plate Tests

Four fungi were used as test organisms, Aspergillus niger USDA-tc-4247, Aspergillus terreus PQMD 82j, Myrothecium verrucaria USDA 1134.2, and Chaetomium globosum USDA 1042.4, from most to least resistant to toxic compounds in the order given. As causes of actual destruction of cotton fabrics (not merely spotting, discoloration, or invasion), A. niger is least important, C. globosum most important. M. verrucaria is a very active decomposer of cellulose.

Exploratory assays involved three-plate replicas over a wide range with two test fungi, A. niger on standard dextrose-inorganic salt agar (Official Screening Method) and C. globosum. Complete assays involved ten-plate replicas on the four test fungi.

Dilution of a standard stock solution of the test compound with agar gave plate concentrations as mg./liter or as parts per million (ppm). When very limited amounts of test compound were available, a layer of noncarbohydrate agar was poured first and allowed to harden, and a thin layer of the fungicide agar was added. A drop of a spore suspension obtained from agar slants was placed in the center of each plate on the hardened agar. The plates were inverted for incubation at 30° C. for 5 to 20 days. After the incubation period, the amount of growth was measured, averaged, and compared with the amount of growth on agar plates without the toxicant.

Fungistatic capacity is expressed in parts per million of test compound required to prevent growth of organism. In some instances it was determined directly from the agar plates, but more frequently from extensions of logistic curves (concentration vs. colony size) or dosage-response curves (concentration vs. percent growth inhibition) on logarithmic scales. Control plates were used in all experiments. Table 1 is a summary of the physical and fungicidal properties of the compounds studied.

#### Cloth Tests

The assays on the protection conferred upon cotton by test compounds began in 1951 with fluorinated quinones, followed shortly by tests with the potent fluorhalo dinitro benzenes.



White 8-oz. cotton duck, or airplane cloth, was the test fabric. It was desized, cut into one-inch squares (or patches), sterilized, and dried. When solvent effect and fungicide absorption were studied, the squares were weighed dry before and after treatment. The fabric was impregnated by exposing it to the test compound in aqueous suspension for two hours or in acetone solution for one hour. After the dried patch had been placed in the center of an agar plate, a spore suspension was seeded as a streak one inch outside the patch margins, and the inverted plates were incubated at 30° C. for a maximum of two weeks. The four test fungi were used, replications ran as high as ten in a series, and the results were usually compared to controls.

#### Thread Protection Tests

When it was found that certain compounds gave excellent protection to cloth squares, the effect upon the tensile strength of the fiber was studied. Cotton parachute webbing thread was the experimental material, and the test fungus was *M. verrucaria*, an active decomposer of cellulose.

Experimental threads 15 inches long were desized, sterilized, dried, and impregnated with a test compound in about the same manner as the cloth squares were treated. The treated threads were placed in plates containing a mineral-salts agar. Small untreated cloth squares were placed in each dish as controls. After inoculation the plates were incubated at 30° C., and after 14 days observations were made and recorded. All threads were removed, sterilized, dried, and sent to Wright Air Development Center where breaking-strength tests were made after the materials were conditioned to 65 percent relative humidity and 70° F.

#### CONSTITUTION-POTENCY RELATIONSHIPS

The data indicate that there are marked differences in fungistatic capacity among classes of compounds, structural isomers, and degree of substitution. In spite of the fairly representative group of compounds studied, it is still quite possible that more potent examples in each class may be found.

An attempt has been made to group the various classes on the basis of potency (ppm required to inhibit growth), and also to call attention to an outstanding class example. The rating is entirely arbitrary, and allowances must be made for overlapping and exceptions.

Very high potency (< 10 ppm): dinitrofluorobenzenes

1-Fluoro-3-bromo-4,6-dinitrobenzene (0.8-1.5 ppm)

High potency (10-200 ppm): fluoronitrophenols, fluorobiphenols, and fluorobiphenol sulfide

2-Nitro-6-fluorophenol (8-23 ppm)

2,2'-Dihydroxy-5,5'-difluorobiphenyl (37-140 ppm)

2,2'-Dihydroxy-5,5'-difluorobiphenyl sulfide (24-95 ppm)

Fair potency (200-400 ppm): fluorophenols, mononitrofluorobenzenes, fluoronitroanilines

2-Bromo-4-fluorophenol (140-210 ppm)

2,4-Difluoronitrobenzene (180-400 ppm)

2-Nitro-4-fluoroaniline (ca. 300 ppm)

Low potency (400-1000 ppm): fluorobenzoic acids, fluoronitrotoluenes, and fluorobenzoquinones

Very low potency ( > 1000 ppm): fluoranisoles, fluorohydroquinones, and diacetate derivatives

It is interesting to note that maximum potency was discovered in the dihalo-dinitrobenzenes when the two halogen substituents are most unlike. A fluorine-iodine combination is reported under "Gladiolus-Disease Control." This unlike-halogen substitution effect on potency appears to be true also in the 2,4-dihalophenols.

The high potency of 2-nitro-6-fluorophenol arouses interesting speculation as to the effectiveness of 2,6 structure.

## APPLICATIONS

### Cotton Thread Protection

The compounds that showed most promise as cotton protectors were the fluorodinitrobenzenes, a fluoronitrophenol, difluorobiphenols, and a difluorobiphenol sulfide. Data on their protection to cotton parachute webbing threads are given in table 2.

An objectionable feature of nitro compounds is their yellow staining of cotton goods. The fluorobiphenols and a corresponding sulfide were prepared in an effort to avoid staining and perhaps achieve higher thermal stability. In breaking-strength experiments, there was no evidence that the compounds caused any significant damage.

### Fungus Resistant Vinyl Plastic

The Materials Laboratory of Wright Air Development Center studied the compounding of 1-fluoro-3-bromo-4,6-dinitrobenzene into polyvinyl chloride plastic tubing. It was learned that complete resistance to the fungi (A. niger, A. flavus, Trichoderma sp. and Penicillium luteum) could be maintained with 0.25 percent of the fungicide in this material. Plastic compounded with the fungicide passed the dielectric strength test of 500 volts per mil thickness, low-temperature (-65° F.) flexing, and inflammability requirements. The plastic was slightly tinted yellow and had a standard tensile-strength test of 2000 lbs./sq. in. and an elongation of 250 to 350 percent.

### Gladiolus-Disease Control

Fusarium rot is the major gladiolus disease in the United States, and in Illinois it is of special concern to the commercial growers in the Kankakee area. In 1953 and 1954, J. L. Forsberg of the Illinois Natural History Survey obtained data at the Kankakee test plots on 3-fluoro-4,6-dinitrophenol, 1,3-difluoro-4,6-dinitrobenzene, 1-fluoro-3-iodo-4,6-dinitrobenzene (m.p. 98-99° C.), and 1-fluoro-3-methyl-4,6-dinitrobenzene.

The gladiolus corms were soaked in water solutions of one part fungicide to 1000 or 2000 parts water for 15 to 60 minutes and then planted. In some cases the fluoro compounds were as effective as the best commercial fungicides.

## TOXICITY

Toxicity data on aromatic fluorine compounds is almost nonexistent. Certain functional groups or compounds without fluorine are toxic, and the introduction of fluorine into such molecules may boost the toxicity. This assumption must be accepted for fluorine compounds until accurate toxicity information becomes available.



Table 1. Summary of Physical and Fungicidal Properties  
(44 fluorine and 7 nonfluorine compounds)

Compound <sup>a</sup>			Concentration as ppm required to prevent growth <sup>b</sup>				
Name and appearance of compound	Empirical Formula	Mol. wt.	M.p. °C	<u>A.</u> <u>niger</u>	<u>A.</u> <u>terreus</u>	<u>M. ver-</u> <u>rucaria</u>	<u>C.</u> <u>globosum</u>
<u>PHENOLS</u>							
Phenol	C <sub>6</sub> H <sub>6</sub> O	94	41 (182°) <sup>d</sup>	> 800	> 800	> 800	
White crystal							
2-Fluorophenol	C <sub>6</sub> H <sub>5</sub> FO	112	f.p. 16.1 (151°-152°) <sup>d</sup>	> 1500	> 1200	> 1200	1200
Amber liquid							
3-Fluorophenol	C <sub>6</sub> H <sub>5</sub> FO	112	f.p. 13.7 (178°) <sup>d</sup>	800	1000	500	500
Amber liquid							
4-Fluorophenol	C <sub>6</sub> H <sub>5</sub> FO	112	48 (185.5°) <sup>d</sup>	600	700	500	> 500
White crystal							
2,4-Difluorophenol	C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> O	130	22.4 (74°/50 mm.) <sup>d</sup>	400	550	400	400
Colorless liquid							
*2-Chloro-4-fluorophenol <sup>c</sup>	C <sub>6</sub> H <sub>4</sub> ClFO	146.5	f.p. 23 (88°/4 mm.) <sup>d</sup>	400	400	350	160
Colorless liquid							
*2-Bromo-4-fluorophenol <sup>c</sup>	C <sub>6</sub> H <sub>4</sub> BrFO	191	42-43 (89°/1 mm.) <sup>d</sup>	140			210
Yellow crystal							
*2-Methyl-4-fluorophenol	C <sub>7</sub> H <sub>7</sub> FO	126	35 (86°/14 mm.) <sup>d</sup>	300			
Colorless liquid							
<u>NITROPHENOLS</u>							
2-Nitrophenol	C <sub>6</sub> H <sub>5</sub> NO <sub>3</sub>	139	45 (214.5°) <sup>d</sup>	50 ← ca.	50% reduction in growth	→ 50	
Yellow crystal				30			10
2-Nitro-4-chlorophenol	C <sub>6</sub> H <sub>4</sub> ClNO <sub>3</sub>	173.5	87				
Yellow crystal							
2-Nitro-4-fluorophenol	C <sub>6</sub> H <sub>4</sub> FNO <sub>3</sub>	157	73.7	40	> 50	50	40

*2,4-Difluoro-6-nitrophenol Yellow crystal	$C_6H_3F_2NO_3$	176	49-50	50	30	40	20	8.4
4-Fluoro-2,6-dinitrophenol Yellow crystal	$C_6H_3FN_2O_5$	202	50	50-55	1000		400	
3-Fluoro-4,6-dinitrophenol Yellow crystal	$C_6H_3FN_2O_5$	202	80	130	180	275	150	
(Also listed under dinitro compounds)								
<u>NITROANILINES</u>								
2-Nitro-4-fluoroaniline Yellow crystal	$C_6H_5FN_2O_2$	156	92.5	300			300	
3-Nitro-4-fluoroaniline Yellow crystal	$C_6H_5FN_2O_2$	156	98					
2-Nitro-5-fluoroaniline Yellow crystal	$C_6H_5FN_2O_2$	156	97	> 400		150	400	
2-Nitro-3,5-difluoroaniline Yellow crystal	$C_6H_4F_2N_2O_2$	174	107-108	600			200	
<u>NITROTOLUENES</u>								
2-Nitro-5-fluorotoluene Yellow crystal	$C_7H_6FNO_2$	155	27-28	1000				
3-Fluoro-4-nitrotoluene Yellow crystal	$C_7H_6FNO_2$	155	53	400				
*3-Fluoro-4,6-dinitrotoluene Yellow crystal	$C_7H_5FN_2O_4$	200	78-79	3.9	7.9	5.5	0.58	
(Also listed under dinitro compounds)								
<u>DINITRO COMPOUNDS</u>								
1-Chloro-2,4-dinitrobenzene Yellow crystal	$C_6H_3ClN_2O_4$	202.5	51 (315°) <sup>d</sup>		> 10	> 10	10	
1-Fluoro-2,4-dinitrobenzene Yellow liquid or solid	$C_6H_3FN_2O_4$	186	25.8 (133°/2 mm.) <sup>d</sup>	5	10	2	4	
1,3-Dibromo-4,6-dinitrobenzene Yellow crystal	$C_6H_2Br_2N_2O_4$	326	117	6			4	

Table 1. (continued)

Name and appearance of compound	Compound <sup>a</sup> Empirical Formula	Mol. wt.	M.p. °C	Concentration as ppm required to prevent growth <sup>b</sup>			
				<u>A. niger</u>	<u>A. terreus</u>	<u>M. ver- rucaria</u>	<u>C. globosum</u>
<b>DINITRO COMPOUNDS (cont.)</b>							
1,3-Dichloro-4,6-dinitro- benzene Yellow crystal	$C_6H_2Cl_2N_2O_4$	237	103	>3	6	1.6	3
1,3-Difluoro-4,6-dinitro- benzene Yellow crystal	$C_6H_2F_2N_2O_4$	204	75	10-15	10-15	10	ca. 15
1-Fluoro-3-chloro-4,6- dinitrobenzene White crystal	$C_6H_2ClFN_2O_4$	220.5	76-77	2-3	ca. 3	2.5	2
1-Fluoro-3-bromo-4,6- dinitrobenzene White crystal	$C_6H_2BrFN_2O_4$	265	91-92	0.8	1.5	0.8	0.8
*1-Fluoro-3-methyl-4,6- dinitrobenzene Pale yellow crystal	$C_7H_5FN_2O_4^e$	200	78-79	3.9	7.9	5.5	0.58
1-Fluoro-3-hydroxy-4,6- dinitrobenzene Pale yellow crystal	$C_6H_3FN_2O_5^f$	202	80	130	180	275	150
3,5-Dinitrobenzotrifluoride Pale yellow crystal	$C_7H_3F_3N_2O_4$	236	49-50	200		200	80
<b>NITRO HALIDES</b>							
2,4-Difluoronitrobenzene Yellow liquid	$C_6H_3F_2NO_2$	159	f.p. 9.75 (207°) <sup>d</sup>	< 400	> 300	180	> 150
2,5-Difluoronitrobenzene	$C_6H_3F_2NO_2$	159	f.p. -11.7 (206.5°) <sup>d</sup>				



2,4-Difluoroanisole Colorless liquid	C <sub>7</sub> H <sub>6</sub> F <sub>2</sub> O	144	f.p.-15.5 (151°) <sup>d</sup>	ca. 1750		
2,4-Difluoro-6-nitroanisole Yellow crystal	C <sub>7</sub> H <sub>5</sub> F <sub>2</sub> NO <sub>3</sub>	189	33-33.5 (66-67°/3 mm.) <sup>d</sup>	ca. 1000		
<b><u>BENZOIC ACIDS</u></b>						
*2,4-Difluorobenzoic acid White crystal	C <sub>7</sub> H <sub>4</sub> F <sub>2</sub> O <sub>2</sub>	158	183-184	350	290	500 525
*2,4,5-Trifluorobenzoic acid White crystal	C <sub>7</sub> H <sub>3</sub> F <sub>3</sub> O <sub>2</sub>	176	97-98	480	475	875 700
<b><u>BENZYL COMPOUNDS</u></b>						
*2,4,6-Trifluorobenzyl chloride <sup>c</sup>	C <sub>7</sub> H <sub>4</sub> ClF	181.5	- (157°) <sup>d</sup>	Very mild fungistatic potency		
Colorless liquid						
*2-Hydroxy-3,5-difluoro- benzyl alcohol	C <sub>7</sub> H <sub>6</sub> F <sub>2</sub> O <sub>2</sub>	160	61-63	> 600		< 600
White crystal						
<b><u>MISCELLANEOUS</u></b>						
*2,2',4,4'-Tetrafluoroazo- benzene	C <sub>12</sub> H <sub>6</sub> F <sub>4</sub> N <sub>2</sub>	254	146-147	No effect at 1000 ppm		
Yellow crystal						
<b><u>QUINONES and DERIVATIVES</u></b>						
2,5-Difluoro-1,4-benzo- quinone	C <sub>6</sub> H <sub>2</sub> F <sub>2</sub> O <sub>2</sub>	144	172.5-173.5	5000	375	375 62.5
Yellow crystal						
*2-Chloro-5-fluoro-1,4- benzoquinone	C <sub>6</sub> H <sub>2</sub> ClFO <sub>2</sub>	160.5	126-127	> 500	> 500	500 > 500
Yellow crystal						
*2-Methyl-5-fluoro-1,4- benzoquinone	C <sub>7</sub> H <sub>5</sub> FO <sub>2</sub>	140	77-78	Very little fungistatic potency		
Yellow crystal						
*2-Chloro-3,6-difluoro-1,4- benzoquinone	C <sub>6</sub> HClF <sub>2</sub> O <sub>2</sub>	178.5	146-147	>> 600		> 500
Yellow crystal						

Table 1. (concluded)

Name and appearance of compound	Compound <sup>a</sup> Empirical Formula	Mol. wt.	M.p. °C	Concentration as ppm required to prevent growth <sup>b</sup>		
				<u>A.</u> <u>niger</u>	<u>A.</u> <u>terreus</u>	<u>M. ver-</u> <u>rucaria</u> <u>C.</u> <u>globosum</u>
<u>QUINONES and DERIVATIVES (cont.)</u>						
*2,5-Dichloro-3,6-difluoro-1,4-benzoquinone (?) Yellow crystal	C <sub>6</sub> Cl <sub>2</sub> F <sub>2</sub> O <sub>2</sub>	213	205 (decomp.)	1600	800	
*2,5-Difluoro-1,4-hydroquinone White crystal	C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> O <sub>2</sub>	146	129.5-130.5	4000	> 500	375
*2,5-Difluoro-1,4-hydroquinone diacetate White crystal	C <sub>10</sub> H <sub>8</sub> F <sub>2</sub> O <sub>4</sub>	230	151-152			1500
2,3,5,6-Tetrachloro-1,4-hydroquinone White crystal	C <sub>6</sub> H <sub>2</sub> Cl <sub>4</sub> O <sub>2</sub>	248	170-171	95	95	35
<u>BIPHENYLS</u>						
*2,2'-Dihydroxy-5,5'-difluorobiphenyl White crystal	C <sub>12</sub> H <sub>8</sub> F <sub>2</sub> O <sub>2</sub>	222	138-139	140	80	110
*3,3'-Difluoro-4,4'-dihydroxybiphenyl White crystal	C <sub>12</sub> H <sub>8</sub> F <sub>2</sub> O <sub>2</sub>	222	189	200	120	127
*2,2'-Dihydroxy-3,3',5,5'-tetrafluorobiphenyl White crystal	C <sub>12</sub> H <sub>6</sub> F <sub>4</sub> O <sub>2</sub>	258	173	230	120	205
*2,2'-Dihydroxy-5,5'-difluorobiphenyl sulfide White crystal	C <sub>12</sub> H <sub>8</sub> F <sub>2</sub> O <sub>2</sub> S	254	119	95	72	26.5
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- <sup>a</sup> Data taken from WADC Tech. Reports 52-214 and 54-148.
- <sup>b</sup> Fungicidal data from L. R. Tehon, Air Force Tech. Report 6518, pts. I, II, III, and IV (Mar. 1951-Jan. 1954).
- <sup>c</sup> Sample borrowed for test purposes, but synthesized on another project.
- <sup>d</sup> Boiling point °C.
- <sup>e</sup> Listed also under nitrotoluenes.
- <sup>f</sup> Listed also under nitrophenols.
- \* New compounds (20 total).



Table 2. Breaking Strengths of Cotton Parachute Webbing Thread Treated with Fungicides and Exposed for 14 Days to Myrothecium Verrucaria.\*

Compound	Treating conc. mg./liter	Fungicide in thread % wt.	Breaking strength lbs.	
			exposed	unexposed
Copper 8 quinolinolate	-	1.05	30.8	30.6
1-Fluoro-2,4-dinitrobenzene	1500	0.17	31.59	30.75
1,3-Difluoro-4,6-dinitrobenzene	1500	0.31	31.03	30.95
1-Fluoro-3-chloro-4,6-dinitro- benzene	2000	0.22	28.85	28.86
1-Fluoro-3-bromo-4,6-dinitro- benzene	1000	0.129	31.58	28.61
1-Fluoro-3-methyl-4,6-dinitro- benzene	1500	0.3	41.9	48.9
2-Fluoro-6-nitrophenol	625	1.63	37.31	37.86
3,3'-Difluoro-4,4'-dihydroxy- biphenyl	1600	2.46	32.66	36.09
5,5'-Difluoro-2,2'-dihydroxy- biphenyl	1600	1.84	34.00	29.20
5,5'-Difluoro-2,2'-dihydroxy- biphenyl sulfide	1000	3.66	34.27	35.31

\*Data based on ten replications.

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